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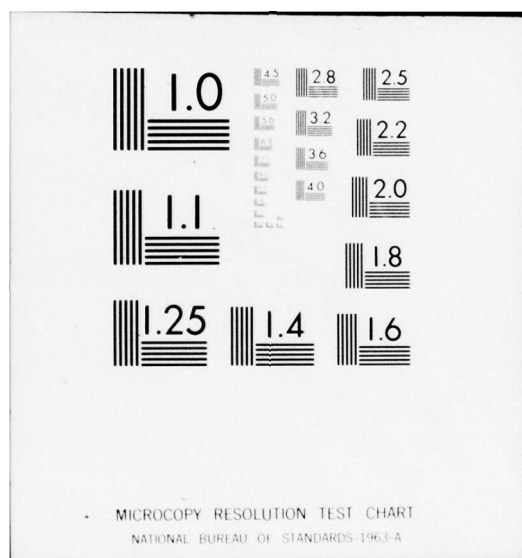
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**THEORETICAL STUDIES OF THE ATMOSPHERIC
TRIATOMIC MOLECULES H_2O , N_2O , NO_2 , CO_2 , O_3 ,
AND THEIR IONS**

by

**Arnold C. Wahl, Walter B. England,
Bruce J. Rosenberg, Darrel G. Hopper,
and Patrick J. Fortune**

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INTRODUCTION

The molecules H_2O , NO_2 , O_3 , CO_2 and N_2O are the dominant triatomic species in the earth's atmosphere. Because of the ready availability of high energy electromagnetic radiation in the upper atmosphere their behavior can be quite diverse. Absorption processes leave the molecules in highly excited and ionized states, and in these cases geometries often differ drastically from the ground state geometries. Furthermore, dissociation and predissociation to atom-diatom asymptotes is common. In order to understand such atmospheric processes, certain fundamental quantities are needed; among these are the definitive location of the excited energy levels and the delineation of reaction mechanisms. These same quantities clearly are necessary for describing the basic chemical behavior of these molecules. In spite of this need, most existing information is inadequate for interpretive or predictive purposes, and understanding atmospheric reactions remains largely guesswork. Our investigation is concerned with providing these energy levels and reaction surfaces through the use of well established *ab initio* techniques. This new theoretical knowledge will be used to advance experimental analysis by participating in a feedback process which historically has proved to provide a deeper understanding of the phenomena involved. We hope that the foundation established by this research will lead to an expanded effort in atmospheric computations at Argonne. Our concerns the past year have largely been excited state characterization and method calibration. Both are prerequisites for any long-range investigation. This is particularly true of the air triatomics because there is so little definitive information presently available. We have also determined linear geometry to bent geometry correlation diagrams. These provide simple ways of predicting reaction possibilities. For example, we found that the four lowest excited states of CO_2^+ are most stable in linear geometries. The fifth excited state was found to be more stable in a bent

geometry. Moreover, in the bent geometry it becomes more stable than three of the four lowest linear ion states, and hence, very likely predissociates the lower energy linear states of CO_2^+ . It is probable that the predissociation just described for CO_2^+ carries over into the Rydberg series that ultimately converge to the ion states in question. Both types of predissociation could be important in atmospheric processes. There are numerous similar examples of important information being provided by this theoretical study.

We have used a variety of quantum chemistry computational techniques in our study of the atmospheric triatomic molecules. Certainly, an integral part of our systematic study is the calibration of various levels and methods of computation. The computational methods used here include: (1) expansion or Roothaan self-consistent field (SCF)¹, (2) traditional configuration interaction (CI) using canonical molecular orbitals², (3) multi-configuration self-consistent field/configuration interaction (MCSCF/CI)^{3,4,5}, and (4) equations-of-motion (EOM)⁶. The computer codes used in our study were (1) the BISONMC⁷ program developed by Das and Wahl for computing SCF and MCSCF wavefunctions, (2) the Battelle-Ohio State CI package developed by Shavitt and co-workers, and (3) the EOM programs developed by McKoy and co-workers at Caltech. The following subsections consist of a molecule-by-molecule summary of the results which are the body of this report.

H₂O. H_2O^+ is the simplest prototype for ion-molecule reactions among the air triatomics. We have computed potential energy surfaces for the ground $^2\text{B}_1$ and the $^2\text{B}_2$ states of H_2O^+ . The results of our vibrational analysis of the $^2\text{B}_1$ surface are in good agreement with experiment. The $^2\text{B}_2$ surface is thought to be predissociated twice, and has a complicated anharmonic vibrational structure. The present level of our results support either of two experimental claims regarding the band origins.

CO₂. Previous theoretical spectra were shown to be of limited accuracy. Experimental assignments based on these are therefore not definitive. Our best correlated spectra are the most accurate available for the lowest multiplet of CO₂. Linear geometry to bent geometry correlation diagrams were also determined for the CO₂, CO₂⁺ and CO₂⁻ systems. Excited states of CO₂ were found to be stable in bent geometries relative to atom-diatom dissociation. Several of the excited linear states in CO₂⁺ are likely to predissociate via a lower-lying bent geometry state. Conflicts with existing CO₂⁻ level assignments were found, and the spectrum was reassigned. Finally, the character of vertically excited states in neutral CO₂ was determined.

O₃. The ongoing controversy over the reaction of ozone with photolyzed freons underlines the important role these triatomics play in atmospheric chemistry. Our correlated results for the vertical excitation energies of O₃ are in very good agreement with experiment, and with other calculations. The O₃⁺ and O₃⁻ calculations provide qualitatively correct electronic spectra for the ions. The ordering of states in O₃⁺ is controversial at present, and we support the ordering X^2A_1 , A^2B_2 and B^2A_2 . Our O₃⁻ spectrum is the only existing data concerning the excitation energies of this ion.

N₂O. The ground state potential energy surface of N₂O⁻ is characterized and related to the ground state potential energy surface of the neutral N₂O molecule by combining theoretical and experimental information. Among the quantities reported are equilibrium geometries, dissociation energies, vertical and adiabatic electron affinities, and the minimum intersection locus of the ground state N₂O and N₂O⁻ surfaces. The results imply that the reaction $O^- + N_2 \rightarrow N_2O + e$ will be strongly enhanced by N₂ vibrational excitation.

NO₂. A definitive theoretical study of NO₂⁵ was performed earlier in our laboratory. Agreement with known experimental results was very good. The energy levels obtained in our present effort provide similar data for NO₂⁺ and NO₂⁻, where little

reliable information is available. Agreement with our previous NO_2 study⁵ is good. We suggest that known spectral complexities in NO_2^+ are due to vibrationally excited states. We also found that existing theoretical NO_2^+ spectra do not consider all of the electronic states in their reported energy ranges, and hence, spectral assignments based on these are unreliable. Our NO_2^- energy levels are the only existing *ab initio* information.

Part of our computational efforts were supported by the CDC6600 computers at Wright-Patterson Air Force Base. We discuss our experience performing large scale molecular calculations remotely on the Wright-Patterson computers in Reference 8 of the publication list given in the next section. Many elements of the effort are general and can be expected to be encountered by other researchers. A summary of the historically important role played by Wright-Patterson is also given.

Personnel Changes. At the end of the last fiscal year, Dr. Richard C. Raffenetti replaced Dr. P. J. Fortune (who joined the staff of the Applied Mathematics Division at Argonne) as project scientist on the Atmospheric Triatomic Molecules project. Dr. Raffenetti received his Ph.D. in physical chemistry from Iowa State University in 1971. He subsequently held post-doctoral appointments at Battelle Memorial Institute and Johns Hopkins University, and most recently was a visiting scientist at the Institute for Computer Applications in Science and Engineering, located at the NASA Langley Research Center.

Acknowledgements. We wish to thank Drs. W. C. Ermler and D. L. Yeager of the University of Chicago for their kind collaboration. We are also grateful to Professor T. O. Tiernan and Dr. R. L. C. Wu of Wright State University for their stimulating experimental collaboration.

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7. G. Das and A. C. Wahl, "BISONMC: A FORTRAN Computing System for Multi-configuration Self-Consistent Field (MCSCF) Calculations on Atoms, Diatoms, and Polyatoms," Argonne National Laboratory Report ANL-7955, 1972.

PUBLICATION LIST

Most of the results described in this report have been published or submitted for publication in the open literature. These papers should be consulted for further details and for discussions of the theoretical methods employed. For convenience, we have assembled a collection of these works which is available upon request from the authors. A list of the papers in question follows.

1. Theoretical Studies of Atmospheric Molecules: SCF and Correlated Potential Surface Results for the X^2B_1 and B^2B_2 States of H_2O^+ , J. Chem. Phys. 65, 2201 (1976).
2. *Ab Initio* Vertical Spectra and Linear-Bent Correlation Diagrams for the Valence States of CO_2 and Its Singly-Charged Ions, J. Chem. Phys. 65, 684 (1976).
3. Theoretical Studies of Atmospheric Triatomic Molecules: Accurate SCF Vertical Spectrum for Valence, Mixed Character, and Rydberg States of CO_2 , J. Chem. Phys., March 1977.
4. Theoretical Studies of Atmospheric Triatomic Molecules: *Ab Initio* Equations of Motion Excitation Energies for Valence States of the Configuration $1\pi_g^3 2\pi_u^1$ in CO_2 , J. Chem. Phys., March 1977.
5. Theoretical Studies of Atmospheric Molecules: *Ab Initio* Vertical Spectra for the Valence States of Ozone and Its Singly-Charged Ions, preprint.
6. Theoretical and Experimental Studies of the N_2O^- and N_2O Ground State Potential Energy Surfaces. Implications for the $O^- + N_2 = N_2O + e$ and Other Processes, J. Chem. Phys., 65, 5475 (1976).
7. Theoretical Studies of Atmospheric Molecules: SCF and Correlated Energy Levels for the NO_2 , NO_2^+ and NO_2^- Systems, Theor. Chim. Acta. submitted.

PUBLICATION LIST, CONT'D.

8. A Case History in Computer Resource Sharing: *Ab Initio* Calculations
Via a Remote Terminal, "Computer Networks and Chemistry," P. Lykos,
ed. (ACS Publications, Washington, 1975).

WATER AND ITS POSITIVE ION

A. Introduction

The equilibrium geometry of the X^1A_1 state of H_2O has been determined by infrared spectroscopy,¹ and various empirical determinations of the internal coordinate force constants have been derived from perturbation analyses of the spectroscopic data.^{2,3,4} The deficiencies in the potential energy constants obtained from *ab initio* self-consistent-field (SCF) calculations are apparent from the resultant computed vibrational energies.^{5,6}

Experimental equilibrium geometries have been obtained for the X^2B_1 , 1^2A_1 , and 1^2B_2 states of H_2O ,⁷⁻¹⁰ but no determinations of potential energy constants have been made yet. Potential energy surfaces for the ground and several excited states of H_2O^+ have been computed using *ab initio* SCF and semi-empirical configuration interaction (CI) techniques.¹¹ The theoretical results¹¹ and photoelectron spectra^{12,13} were subsequently combined to discuss the predissociation and analyze the vibrational structure of the 1^2B_2 state, and it was concluded that the 2B_2 state was predissociated twice.⁹ The position of the appearance potential of the OH^+ ion being just above the 1^2B_2 adiabatic ionization potential is also related to the predissociation of the upper vibrational levels of that state. The coupling of the 1^2B_2 and 1^2A_1 components of the $1^2A'$ state adds to the complexity of the 2B_2 surface.

B. Neutral H_2O

One of the authors (BJR) has previously computed *ab initio* SCF and CI potential energy surfaces in the neighborhood of the energy minimum for the X^1A_1 state of H_2O .¹⁴ The energy surface

was represented by a quartic Taylor series expansion, in terms of the internal coordinates $(\Delta R_1, \Delta R_2, \Delta \theta)$, of the form⁶

$$\begin{aligned}
 E = E_e &+ K_4(\Delta R_1^2 + \Delta R_2^2) + K_5\Delta\theta^2 + 2K_6\Delta R_1\Delta R_2 \\
 &+ 2K_7(\Delta R_1 + \Delta R_2)\Delta\theta + K_8(\Delta R_1^3 + \Delta R_2^3) + K_9\Delta\theta^3 \\
 &+ 3K_{10}(\Delta R_1 + \Delta R_2)\Delta R_1\Delta R_2 + 3K_{11}(\Delta R_1^2 + \Delta R_2^2)\Delta\theta \\
 &+ 6K_{12}\Delta R_1\Delta R_2\Delta\theta + 3K_{13}(\Delta R_1 + \Delta R_2)\Delta\theta^2 \\
 &+ K_{14}(\Delta R_1^4 + \Delta R_2^4) + K_{15}\Delta\theta^4 + 4K_{16}(\Delta R_1^2 + \Delta R_2^2)\Delta R_1\Delta R_2 \\
 &+ 6K_{17}\Delta R_1^2\Delta R_2^2 + 4K_{18}(\Delta R_1^3 + \Delta R_2^3)\Delta\theta \\
 &+ 12K_{19}(\Delta R_1 + \Delta R_2)\Delta R_1\Delta R_2\Delta\theta + 6K_{20}(\Delta R_1^2 + \Delta R_2^2)\Delta\theta^2 \\
 &+ 12K_{21}\Delta R_1\Delta R_2\Delta\theta^2 + 4K_{22}(\Delta R_1 + \Delta R_2)\Delta\theta^3
 \end{aligned} \tag{1}$$

The resultant force constants along with various empirically-derived sets are given in Table I. Recently, in collaboration with workers at other laboratories, these potential energy constants have been used in a variation-perturbation method⁶ to compute vibrational energy levels.¹⁵ The calculated and experimentally-observed¹ energy levels are compared in Table II. The importance of including correlation effects in the wavefunction when computing potential energy surfaces is evident from the significant improvement in the CI harmonic force constants (K_4 - K_7) and vibrational energies compared to the SCF values. The CI vibrational energies show an average error of $\sim 4\%$.

C. Positive Ion H_2O^+

Ab initio SCF and multi-configuration self-consistent field/ configuration interaction (MCSCF/CI) potential energy surfaces, in the neighborhood of the energy minima, were computed for the X^2B_1 and \tilde{B}^2B_2 states of H_2O^+ . The energies were fit to a cubic Taylor series expansion (Eq. (1), truncated after K_{13}), and the resulting equilibrium geometries and force constants are presented in Table III. The computed equilibrium geometries are seen to be consistent with what one would expect from Walsh's rules. The potential energy constants were then input to a vibrational analysis program⁶ to compute harmonic frequencies, Table IV, and second-order corrected vibrational energies, Table V.

From Table V, it is clear that the computed vibrational results for the 2B_1 state are in good agreement with available experimental data.^{7,12,13,16} However, it is seen that the lowest symmetric and asymmetric stretching frequencies are stable to only about 10% as one proceeds from the harmonic to cubic fits, i.e., Table IV to Table V; the lowest bending frequency changes very little which is consistent with the fact that the dominant cubic term is K_8 .

The results for all the vibrational frequencies of the 2B_2 state exhibit significant changes as the effects of cubic terms are added. This is to be expected at the outset, as the anharmonic nature of the progression of peaks in the photoelectron spectrum has been observed.¹³ It is interesting to note that the value quoted in Ref. 13 for the lowest bending excitation agrees with that from the cubic analysis, while the harmonic results agree with those of Ref. 12.

D. Future Goals

Because of the marked changes in the vibrational energies on including cubic anharmonic terms in the potential energy expansion, it is necessary to investigate the effects of adding quartic and higher terms in the expansion. In an attempt to resolve the disputed assignments of the 2B_2 band origins of the photoelectron spectra of H_2O , higher order perturbation theory, or a variational approach^{17,18} will also be considered.

In order to study the predissociation of the 2B_2 state, it will be necessary to compute potential surfaces for the $1^4A''$ and $2^2A''$ states as well as additional regions of the 2B_2 surface. A complete understanding of the 2B_2 state will also require an examination of its coupling through asymmetric distortion with the 1^2A_1 state.

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Table I. Equilibrium Geometry and Force Constants for the X^1A_1 State of the Water Molecule^a

Constant	SCF ^b	C1 ^b	SO ^c	KM(I) ^d	KM(II) ^d	HMS ^e
R_e	1.77604	1.80040	1.8089	1.8089	1.8089	1.8089
θ_e	106.085°	104.930°	104.52°	104.52°	104.52°	104.52°
E_e	-76.06497650(2)	-76.33986662(2)	-	-	-	-
K_4	0.31451(3)	0.28504(1)	0.271(1)	0.2715	0.2715	0.2715
K_5	0.088652(6)	0.084685(8)	0.085(4)	0.0800	0.0800	0.0799
K_6	-0.00212(2)	-0.002661(9)	-0.004(1)	-0.0032	-0.0032	-0.0032
K_7	0.014695(3)	0.015655(4)	0.029(9)	0.0132	0.0132	0.0133
K_8	-0.3745(6)	-0.3462(2)	-0.33(2)	-0.339(2)	-0.36(2)	-0.34(5)
K_9	-0.03022(8)	-0.02711(4)	-0.045(3)	-0.029(2)	-0.027(4)	-0.03(1)
K_{10}	0.0000(2)	-0.00025(6)	-0.002(6)	-0.004(2)	0.006(6)	0.00(3)
K_{11}	-0.0007(3)	-0.0008(1)	-0.01(1)	0.0034(6)	0.005(1)	0.004(6)
K_{12}	-0.0057(3)	-0.0055(1)	-0.007(4)	-0.0071(1)	-0.0049(4)	-0.004(9)
K_{13}	-0.00602(3)	-0.00601(2)	-0.017(1)	0.006(8)	0.01(1)	-0.004(6)

Constant	SCF ^b	CI ^b	SO ^c	KM(I) ^d	KM(II) ^d	HMS ^e
K ₁₄	0.277(3)	0.277(4)	0.27(7)	0.302(6)	0.36(3)	0.3(1)
K ₁₅	-0.0094(5)	-0.0069(6)	-0.01(3)	0.00(4)	0.00(4)	-0.001(6)
K ₁₆	-0.0004(6)	-0.0001(8)	0.006(8)	0.004(3)	-0.01(1)	-0.00(4)
K ₁₇	0.0004(5)	0.0004(6)	0.007(7)	0.004(4)	0.00(1)	0.00(2)
K ₁₈	-0.002(3)	-0.002(3)	-0.06(6)	-	-	-
K ₁₉	0.0005(9)	0.001(1)	-0.02(3)	-	-	-
K ₂₀	-0.0009(6)	-0.0008(7)	-0.01(2)	-0.018(9)	-0.03(1)	-0.0037(6)
K ₂₁	0.0015(5)	0.0017(6)	-0.00(2)	-0.003(9)	-0.01(1)	0.001(4)
K ₂₂	0.0036(1)	0.0031(2)	-0.01(3)	-	-	-

^a All quantities in atomic units, and are referred to Eq. (1).

^b B. J. Rosenberg, W. C. Ermler, and I. Shavitt, J. Chem. Phys. 65, 4072 (1976). Error limits, in parenthesis, are 3 x statistical standard deviations in the last significant digit.

^c D. F. Smith and J. Overend, Spectrochimica Acta 28A, 471 (1972). Error limits, in parenthesis, are 3 x statistical standard deviations in the last significant digit.

^d K. Kuchitsu and Y. Morino, Bull. Chem. Soc. Japan 38, 814 (1965). Error limits, in parenthesis, are 3 x uncertainties in the last significant digit. Constants K₁₈, K₁₉ and K₂₂ were constrained to be zero. Columns (I) and (II) are anharmonic force constants for H₂O and D₂O, respectively.

^e A. R. Hoy, I. M. Mills and G. Strey, Mol. Phys. 24, 1265 (1972). Error limits, in parenthesis, are the estimated uncertainties in the last significant digit. Constants K₁₈, K₁₉ and K₂₂ were constrained to be zero.

Table II. Energies of low-lying vibrational states of the X^1A_1 state of H_2O^a .

Vibrational State ^b	SCF	CI	Expt. ^c
(0,0,0)	5008	4777	4634
(1,0,0)	8968	8537	8290
(0,1,0)	6757	6463	6231
(0,0,1)	9077	8646	8388
(2,0,0)	12842	12212	11861
(0,2,0)	8473	8120	7794
(0,0,2)	13053	12422	12048
(1,1,0)	10716	10223	9871
(1,0,1)	12866	12339	11879
(0,1,1)	10849	10354	9965

^aAll energies in cm^{-1} .

^bThe vibrational modes are labeled in the standard fashion, i.e., 1-2-3 correspond to symmetric stretch - bend - asymmetric stretch, respectively.

^cW. S. Benedict, N. Gailar, and E. K. Plyler, J. Chem. Phys. 24, 1139 (1956).

Table III. Equilibrium geometry and force constants for the X^2B_1 and \tilde{B}^2B_2 states of H_2O^+ .^a

Constant	X^2B_1		\tilde{B}^2B_2	
	SCF	MCSCF/CI	SCF	MCSCF/CI
R_e	1.8624	1.9037	2.0846	2.1544
θ_e	111.41°	108.50°	58.45°	54.96°
E_e	-75.645647(1)	-75.723280(1)	-75.476289(8)	-75.55451(1)
K_4	0.241(2)	0.2111(7)	0.114(5)	0.092(5)
K_5	0.0725(7)	0.0742(2)	0.120(2)	0.152(2)
K_6	0.002(1)	-0.0007(5)	0.026(4)	0.020(3)
K_7	0.0073(7)	0.0088(2)	0.029(2)	0.034(1)
K_8	-0.257(9)	-0.25(1)	-0.13(8)	-0.1(2)
K_9	-0.029(3)	-0.028(4)	-0.18(3)	-0.21(4)
K_{10}	0.000(2)	0.000(3)	-0.01(2)	-0.01(5)
K_{11}	-0.00(1)	-0.01(1)	-0.0(1)	-0.01(4)
K_{12}	-0.004(8)	0.00(1)	-0.01(8)	-0.00(2)
K_{13}	-0.007(3)	-0.006(4)	-0.05(3)	-0.05(2)

^aAll quantities in atomic units and are referred to Eq. (1). Numbers in parenthesis following force constant values are three times the statistical standard deviation in the last digit reported.

Table IV. Harmonic frequencies of the X^2B_1 and B^2B_2 states of H_2O^+ .^a

Frequency	X^2B_1		\tilde{B}^2B_2	
	SCF	MCSCF/CI	SCF	MCSCF/CI
ω_1	3635	3388	2872	2651
ω_2	1538	1518	1617	1669
ω_3	3685	3469	2178	1975

^aAll frequencies in cm^{-1} .

Table V. Energies of low-lying vibrational states of the X^2B_1 and B^2B_2 states of H_2O^+ .^a

Vibrational State ^b	X^2B_1		B^2B_2	
	SCF	MCSCF/CI	SCF	MCSCF/CI
(0,0,0)	4321	4054	3152	3009
(1,0,0) ^{c,d,e}	7687	7102	5512	5303
(0,1,0) ^{c,d,e,f}	5829	5543	4510	4473
(0,0,1)	7726	7172	4994	4742
(2,0,0)	10922	9982	7737	7489
(0,2,0)	7312	7013	5848	5920
(0,0,2)	10988	10115	6728	6386
(1,1,0)	9185	8584	6482	6484
(1,0,1)	10819	9882	6989	6821
(0,1,1)	9226	8650	6261	6114

^aAll energies in cm^{-1} .^bVibrational modes are labeled in the standard fashion, i.e., 1-2-3 correspond to symmetric stretch-bend-asymmetric stretch, respectively.^cC.R. Brundle and D.W. Turner, Proc. Roy. Soc. London A307, 27 (1968). Excitation energies from (0,0,0) are: $\Delta E(1,0,0) = 3200\text{ cm}^{-1}$, $\Delta E(0,1,0) = 1380\text{ cm}^{-1}$ for X^2B_1 state, and $\Delta E(1,0,0) = 2990\text{ cm}^{-1}$, $\Delta E(0,1,0) = 1610\text{ cm}^{-1}$ for B^2B_2 state.^dA.W. Potts and W.C. Price, Proc. Roy. Soc. London A326, 181 (1972). Excitation energies from (0,0,0) are $\Delta E(1,0,0) = 3220\text{ cm}^{-1}$, $\Delta E(0,1,0) = 1370\text{ cm}^{-1}$ for X^2B_1 state, and $\Delta E(1,0,0) = 2985\text{ cm}^{-1}$, $\Delta E(0,1,0) = 1370\text{ cm}^{-1}$ for B^2B_2 state.^eL. Karlsson, L. Mattsson, R. Jadrny, R. G. Albridge, S. Pinchas, T. Bergmark, and K. Siegbahn, J. Chem. Phys. 62, 4745 (1975). Excitation Energies from (0,0,0) are $\Delta E(1,0,0) = 3242\text{ cm}^{-1}$, $\Delta E(0,1,0) = 1428\text{ cm}^{-1}$ for X^2B_1 state, and $\Delta E(1,0,0) = 2928\text{ cm}^{-1}$, $\Delta E(0,1,0) = 1524\text{ cm}^{-1}$ for B^2B_2 state.^fH. Lew and I. Heiber, J. Chem. Phys. 58, 1246 (1973). Excitation energy from (0,0,0) is $\Delta E = (0,1,0) = 1412\text{ cm}^{-1}$ for X^2B_1 state.

CARBON DIOXIDE AND ITS IONS

A. Introduction

Simple Walsh-Mulliken predictions^{1,2} anticipate much of the interesting and varied behavior of the CO_2 , CO_2^+ , CO_2^- molecules in a qualitative sense. A linear equilibrium geometry is predicted for ground state CO_2 , while many of the low-lying excited states of CO_2 are predicted to be bent. Under these conditions, the electronic spectrum and possible attachment, detachment, dissociation, etc., mechanisms may vary widely with geometry. A similar prediction is made for CO_2^+ . In CO_2^+ , however, there should also be many low-lying and as yet unobserved states which arise from the large number of unoccupied molecular orbitals. The negative ion CO_2^- is predicted to have a bent equilibrium geometry. Again because of the large number of unoccupied valence molecular orbitals, many low-lying excited states are anticipated. A large number of these are expected to be resonance states, inasmuch as CO_2 will not bind an electron in many cases.

Apart from qualitative considerations such as those just outlined, rather little information exists concerning the electronic states of the $\text{CO}_2/\text{CO}_2^+/\text{CO}_2^-$ systems. Definitive information consists of Dixon's assignment^{3,4} of the $1\ ^1\text{B}_2 \leftarrow 1\ ^1\text{A}_1$ transition in CO_2 , and the four lowest vertical ionization potentials of CO_2 .⁵ Rydberg series in CO_2 have also been accurately measured,⁶ but the nature of the Rydberg orbitals involved, and hence the symmetry of the electron states, is unknown. The lower-lying electronic states of CO_2 are complicated by the possibility of valence-Rydberg

mixing, and almost nothing is known about these states. Even the lowest valence type states have not been definitely analyzed experimentally, and existing theoretical investigations^{7,8} of these states have not employed sufficient accuracy for the results to be accepted without question.

With the exception of a semiempirical study,⁹ little theoretical work has been done on the electronic states of CO_2^- . Subsequent *ab initio* work^{10,11} has shown the semiempirical results to be even qualitatively incorrect as regards the stability of ground state CO_2^- relative to ground state CO_2 . The semiempirical model predicted that the ground state potential energy surfaces of CO_2 and CO_2^- do not intersect, whereas *ab initio*^{10,11} and experimental¹² findings showed that the surfaces do intersect. As a consequence, the assignments based on the semiempirical model are open to questions.

B. Linear and Bent Geometry Correlation Diagrams

The changes in the $\text{CO}_2/\text{CO}_2^+/\text{CO}_2^-$ electronic states upon molecular bending were determined by two sets of computations. First, self-consistent-field (SCF) calculations were carried out at the equilibrium bondlength ($R_{\text{CO}} = 2.1944$ bohrs) of ground state $\text{CO}_2 (\text{X}^1\Sigma_g^+)$. Second, the bondlength R_{CO} was held fixed, and SCF calculations performed at a bond angle close to estimates^{11,12} of the equilibrium bond angle of ground state $\text{CO}_2^- (\text{X}^2\text{A}_1)$, $\angle \text{OCO} = 130^\circ$. Results for both geometries were obtained for each of the molecules $\text{CO}_2/\text{CO}_2^+/\text{CO}_2^-$.

Neutral CO_2

Figure 1 shows the linear and bent geometry spectra for the lowest-lying valence states of CO_2 . Most of the excited states

shown will have minimal energies for bent geometries. Electronic spectra which involve bent geometry CO_2 molecules will be clearly very different from the vertical (linear geometry) spectrum of CO_2 .

The bent molecule energy levels support Dixon's assignment of B_2 symmetry.^{3,4} A total of five bent states (1A_1 , 3B_2 , 3A_2 , 1A_2 , 1B_2) are bound relative to the lowest SCF asymptote, $\text{CO}(^1\Sigma^+) + \text{O}(^3P)$.

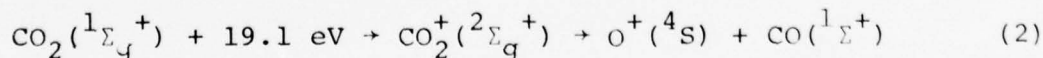
The diagram partially supports an earlier mechanism¹³ for the reaction



in which the surfaces 1B_2 and 3B_2 are assumed to cross, and partially supports a mechanism¹⁴ in which the two surfaces are not assumed to cross. In terms of the former mechanism, the predicted 1B_2 surface appears to overestimate the well depth.⁴ A binding energy of ~ 2 eV is predicted for 3B_2 relative to $\text{O}(^3P) + \text{CO}(^1\Sigma^+)$, and this concurs with both earlier kinetic studies.^{13,14}

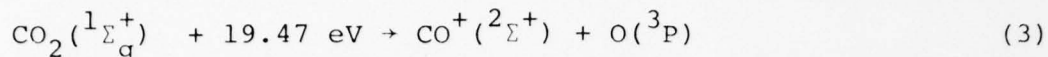
Positive Ion CO_2^+

Figure 2 shows the linear-bent correlation diagram for CO_2^+ . Known and unknown excited electronic states overlap over a wide energy range. The $^4\Pi_u$ state is substantially stabilized upon bending, where it becomes 4B_1 , and is capable of predissociating lower-lying states. Dissociation of CO_2^+ has been shown¹⁵ to proceed by predissociation of the $^2\Sigma_g^+$ state



Fluorescence from $^2\Sigma_g^+$ is not observed, and predissociation occurs from the ground vibrational state of $^2\Sigma_g^+$. Our results imply that the $^4\Pi_u$ surface is capable of predissociating $^2\Sigma_g^+$ in the Franck-Condon region of the ground vibrational state. It is furthermore

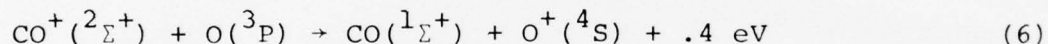
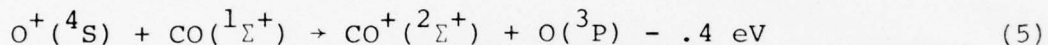
possible to correlate the ${}^4\Pi_u$ CO_2^+ and O^+ , CO asymptote symmetries with a C_s reaction path. The observed reaction¹⁶



is suggested by our results to proceed via a linear reaction path, again involving predissociation by the ${}^4\Pi_u$ surface. The reaction



is reported to be fast. Our results favor the asymptotes $\text{CO}^+({}^2\Sigma^+)$, $\text{O}({}^3\text{P})$, since these connect adiabatically to the reagent states via the $\text{CO}_2^+({}^4\Pi_u)$ surface. The set of reverse reactions



have been observed.¹⁷⁻¹⁹ According to our results, the reagents of Reaction (5) would approach on the ${}^4\text{A}''$ (${}^4\Pi_u$) surface, to which they correlate in C_s symmetry. Products would then be formed by population of the ${}^4\text{A}'$ (${}^4\Pi_u$) surface. The exothermic Reaction (6) has been observed to be fast,¹⁹ and could occur by the reverse of the process described for Reaction (5). However, there are necessary surface crossings in the asymptotic surfaces, and for this reason alone the reaction should be fast.

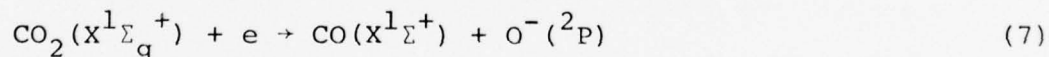
Negative Ion CO_2^-

The linear-bent correlation diagram for CO_2^- is presented on Figure 3. As was found for CO_2^+ , known and unknown excited electronic states overlap over a wide energy range. The ${}^4\Pi_g$, ${}^2\Phi_g$ and ${}^2\Pi_g$ can all be expected to predissociate the ${}^2\Sigma_u^+$ and ${}^2\Sigma_g^+$ states, and, in some cases, possibly the ${}^2\text{B}_1$ Renner split component of

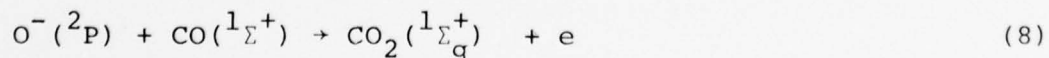
$^2\Pi_u$. We predict that $CO_2^-(X^2A_1)$ is metastable, in agreement with other *ab initio* results,^{10,11} and with experiment,¹² but in direct contradiction with semiempirical findings.⁹ Our assignments of the excited states also differ from the semiempirical assignments. We find the $^2\phi_g$ state to lie above $^2\Sigma_u^+$, whereas the semiempirical study finds just the opposite. As a consequence, our correlation diagram supports different predissociation and reaction mechanism possibilities from those that could be deduced from the semiempirical results.

We predict a vertical electron affinity of ~ -4 eV, which agrees with experimental estimates.²⁰ The adiabatic electron affinity is estimated to be ~ -1 eV on the basis of our results, in reasonable agreement with experiment.²¹⁻²⁴

The overall features of the correlation diagram suggest that intersection of the ground state CO_2/CO_2^- potential energy surfaces will be similar to the intersection of the isoelectronic N_2O/N_2O^- potential surfaces which we describe in detail in a later section of this report. We therefore predict that the dissociative attachment



will yield vibrationally excited $CO(X^1\Sigma^+)$. This agrees with experimental suggestions.²⁵ The associative detachment



should also be overall similar to the corresponding O^- , N_2 detachment process. However, the electron affinities of CO_2 appear to be significantly larger than those of N_2O , and this may account for the fact that Reaction (8) is moderately fast,²⁷⁻³⁰ whereas

the corresponding O^- , N_2 detachment is slow.

C. Valence States, Mixed Character States, and Rydberg States in Neutral CO_2

An interesting feature in the electronic spectra of CO_2 and other molecules is that the electronic states fall into three qualitatively different classes. The first class consists of valence states, whose spacial extents are similar to that of ground state $CO_2(X^1\Sigma_g^+)$. The second class consists of mixed character, or large states, whose spacial extents are much beyond the valence state region. Rydberg states make up the third class, viz. Those satisfying the Rydberg formula⁶

$$\Delta E_i = 13.605/[n^*(E)]^2 \quad (\text{units are eV}) \quad (9)$$

where

$$\Delta E_i = E(\text{Neutral State}) - E(\text{Parent Ion State}) \quad (10)$$

and $n^*(E)$ is the effective quantum number. In the case of mixed and Rydberg states, the character (spacial extent, validity of Equation (9)) is determined by a single outer occupied orbital.

We computed an accurate self-consistent-field (SCF) vertical spectrum for CO_2 in order to determine which of the states were valence, mixed character, or Rydberg states. All single electron excitations out of the four highest occupied molecular orbitals (MO's) into the five unoccupied MO's $2\pi_u$, $5\sigma_g$, $4\sigma_u$, $1\delta_g$ and $2\pi_g$ were included, giving a total of 60 electronic states. The energy levels are shown on Figure 4. Orbital energies, orbital second moments, and the second moment analog of Equation (10),

$$\Delta Q_i = Q(\text{Neutral State}) - Q(\text{Parent Ion State}) \quad (11)$$

were computed. Effective quantum numbers for the mixed and Rydberg states were calculated from Equation(9), and from the hydrogenic formula

$$n^*(\bar{r}^2) = [0.5b_\ell + 0.5(b_\ell^2 + 1.6\bar{r}^2)^{\frac{1}{2}}]^{\frac{1}{2}} \quad (12)$$

with

$$b_\ell = 0.6[\ell(\ell+1) - 1/3] \quad (13)$$

The angular quantum numbers, ℓ , could be determined without ambiguity from the character of the MO in question. The SCF computations give representations of five MO's ($2\pi_u$, $5\sigma_u$, $4\sigma_u$, $1\delta_g$ and $2\pi_g$) which are unoccupied in ground state $\text{CO}_2(X^1\Sigma_g^+)$. The $5\sigma_g$ is always a large, or mixed character MO, and hence each electronic state in which the $5\sigma_g$ is occupied is a mixed character state. This contradicts earlier, less accurate, *ab initio* findings.^{7,8} The $4\sigma_u$, $1\delta_g$ and $2\pi_g$ are always Rydberg MO's, and thus electronic states in which one of these MO's is occupied are always Rydberg states. The $2\pi_u$ MO is fundamentally different, and can have either valence or Rydberg character. It has Rydberg character in the V-states $1\Sigma_u^+$ and $1\Sigma_g^+$, and otherwise has valence character.

The SCF and experimental Rydberg series are compared in Table 1. All experimental Rydberg levels with $n^* \leq 3$ have been included, since this is the range of n^* we have considered theoretically. The agreement between theory and experiment is very good, and the symmetries of the electronic states corresponding to the observed series are here definitely assigned for the first time. However, none of the SCF Rydberg levels gives the experimentally observed

$n^* = 2.70$. Preliminary analysis suggests that the $6\sigma_g$ MO is involved, which we did not include in the present work.

To a good approximation, many Rydberg state characteristics depend only on the Rydberg MO. Average values for the Rydberg MO's are reported in Table 2. Each row of the table contains the average value for a given Rydberg MO. For example, the second entry in the first row is the average of all the $2\pi_g$ MO orbital energies we computed. Deviations about the averages are at worst a few percent, and usually smaller. Note that the two different theoretical ways of computing effective quantum numbers, $n^*(E)$ and $n^*(\bar{r}^2)$, are in close agreement.

D. Vertical Spectrum Including Electron Correlation for
Valence States of the Configuration $1\pi_g^3 2\pi_u^1$ in CO_2

The configuration $1\pi_g^3 2\pi_u^1$ can be angular momentum coupled to form the electronic states $1,3\Sigma_u^+$, $1,3\Sigma_u^-$, $1,3\Delta_u$. The V-state $1\Sigma_u^+$ is Rydberg in character, and will not be considered here. By allowing valence and Rydberg character to mix, the remaining states were found to be valence states. Definitive experimental state assignments for these valence states have not been given, and previous theoretical treatments^{7,8} of them have been of only modest accuracy. In the overall spirit of our theoretical project, namely, method calibration and evaluation, we have therefore performed several theoretical calculations of the electronic states in question which employ successively more accurate approximations, all of which are more accurate than the existing theoretical data. We first performed self-consistent-field (SCF) and multiconfiguration self-consistent-field calculations, followed by configuration

interaction, (MCSCF/CI) with accurate (polarized) expansion sets. These differed markedly from the existing theoretical spectra, implying that the latter could only be accurate if cancellation of expansion set and correlation energy errors occurred. We next carried out equations-of-motion (EOM) calculations with accurate polarized expansion sets. The EOM calculations incorporate a more complete treatment of the correlation energy, and provide the most accurate theoretical spectrum currently available. We find for the EOM vertical excitation energies

$^3\Sigma_u^+$:	7.41 eV
$^3\Delta_u$:	8.13 eV
$^3\Sigma_u^-$:	8.45 eV
$^1\Sigma_u^-$:	8.51 eV
$^1\Delta_u$:	8.51 eV

Interestingly enough, these values are fortuitously close to the existing limited accuracy theoretical spectra.

E. Future Goals

Potential energy surface priorities begin with the ground state surface of neutral CO_2 . More information exists³¹⁻³⁹ for this potential surface than for any others in the molecules $\text{CO}_2/\text{CO}_2^+/\text{CO}_2^-$. We will exploit this to simultaneously assess our own surfaces and several ways of computing triatomic force constants. Armed with a suitably calibrated method, we will then probe the ground state surface of neutral CO_2 to whatever extent is necessary. Proper dissociation will be especially emphasized. Beyond this we will investigate CO_2^+ potential surfaces, which are so important in ionospheric ion-molecule reactions. An investigation

of the intersection of the $\text{CO}_2/\text{CO}_2^-$ ground state potential surfaces is also envisioned.

Investigation of neutral CO_2 excited states will also continue. Locating the lowest $^1\Delta_u$ and $^1\Pi_g$ states relative to one another appears to be needed for understanding possible reaction mechanisms. Both are optically forbidden states, and hence are difficult to probe experimentally. Our current theoretical results imply that the states are nearly degenerate. The Rydberg character of the excited states as a function of geometry is likewise of interest. If the Rydberg character changes with the geometry, the state in question may not behave like its parent ion state, and hence its role in chemical reactions cannot be reliably predicted based on ion states.

Very little is known about the ionization of inner electrons in CO_2 , and also of shake-up ionization. The $^4\Sigma_g^-$ ion state may have predissociation capabilities similar to the $^4\Pi_u$ ion state that we discussed in this report. The location of the $^4\Sigma_g^-$ state, and of other unknown CO_2^+ states, will therefore be determined.

There may be low-lying states of CO_2^- which lie in the energy range that we reported here. Using methods similar to those we describe for O_3^- elsewhere in this document, a closer scan of possible excited states will be undertaken. Ultimately, a re-analysis of the experiments as given in Reference 9 is required with reliable *ab initio* curves.

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Table 1. Rydberg states and MO configurations for CO₂. The experimental results were taken from Ref. 6, where references to the original work can be found.

Ion State	Rydberg State	MO Configuration	δ^a		n^*		ΔE_i (eV)	
			Expt.	SCF	Expt.	SCF	Expt.	SCF
$X^2\Pi_g$	$1\Sigma_u^+$	$1\pi_g^{-1}p_\pi$	0.65	0.65	2.35	2.35	2.46	2.46
	$1,3\Pi_u$	$1\pi_g^{-1}p_\sigma$	0.57	0.53	2.43	2.47	2.30	2.23
$A^2\Pi_u$	$1,3\Sigma_g^+, 1,3\Delta_g$	$1\pi_g^{-1}d_\pi$	0.97	0.96	3.03	3.04	1.48	1.47
	$1,3\Phi_u, 1,3\Pi_u$	$1\pi_u^{-1}d_\delta$	0.093	0.05	2.907	2.95	1.61	1.56
$B^2\Sigma_u^+$	$1,3\Pi_u$	$3\sigma_u^{-1}d_\pi$	0.90	0.94	3.10	3.06	1.42	1.45
			0.30		2.70		1.87	
$C^2\Sigma_g^+$	$1,3\Delta_g$	$4\sigma_g^{-1}d_\delta$	0.05	0.00	2.95	3.00	1.56	1.51

^a Quantum defect.

Table 2. Average Rydberg state expectation values.

MO	ΔE_i^a	$-\epsilon^{a,b}$	$\bar{r}^{2^{c,d}}$	$\bar{z}^{2^{c,d}}$	$\bar{x}^{2^{c,d}}$	ΔQ_i^e	$q^{e,f}$	$n^*(E)$	$n^*(\bar{r}^2)$
$2\pi_g(d_\pi)$	1.45	1.45	146.3	62.7	41.8	-28.0	-28.2	3.07	3.09
$1\delta_g(d_\delta)$	1.53	1.53	120.0	17.2	51.4	46.0	46.1	2.98	2.98
$4\sigma_u(p_\sigma)$	2.23	2.25	84.0	50.1	17.0	-43.8	-44.6	2.47	2.51
$2\pi_u(p_\pi)$	2.46	2.49	66.3	13.2	26.6	17.8	18.0	2.35	2.38

^aUnits are eV.

^b ϵ = orbital energy of Rydberg MO.

^cRydberg MO expectation value, origin at C and bonds along z-axis.

^dUnits are a_0^2 , a_0 = Bohr radius.

^eUnits are esu-cm² x 10²⁶.

^fRydberg MO second moment.

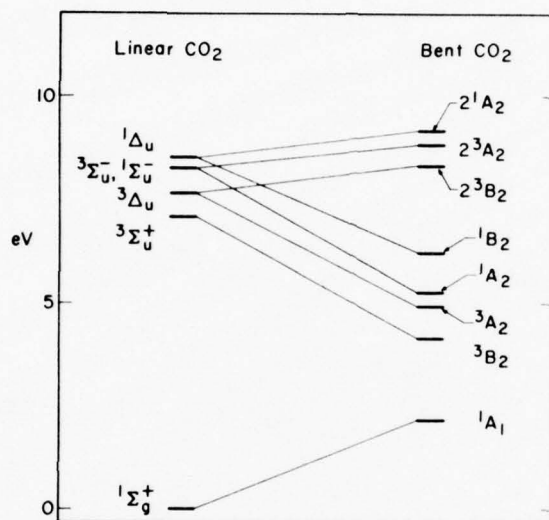


Fig. 1.
SCF State Correlation Diagram for
Linear and Bent CO₂. The Energy
Zero is CO₂($1\Sigma_g^+$).

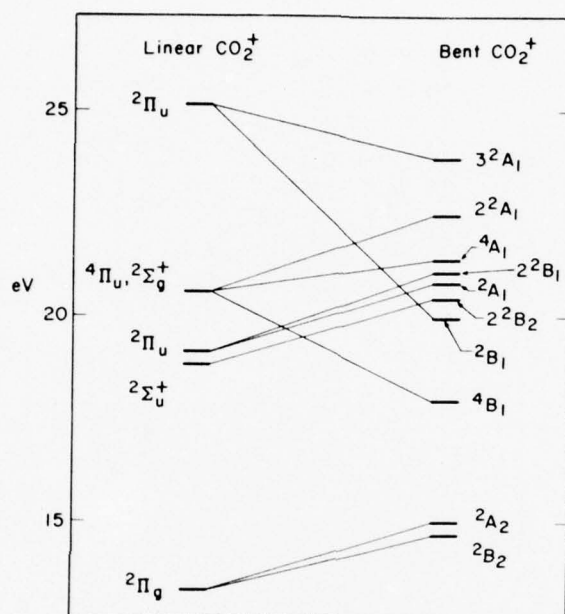


Fig. 2.
SCF State Correlation Diagram for
Linear and Bent CO_2^+ . The Energy
Zero is $\text{CO}_2(1\Sigma_g^+)$.

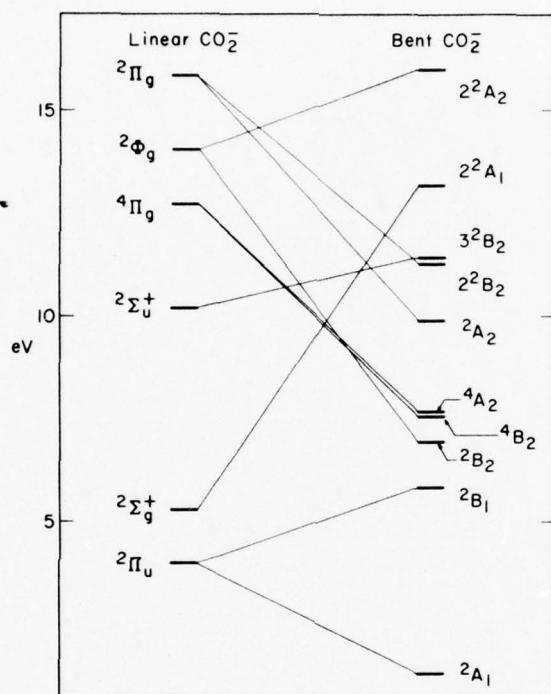


Fig. 3.

SCF State Correlation Diagram for Linear and Bent CO₂. The Energy Zero is CO₂(${}^1\Sigma_g^+$).

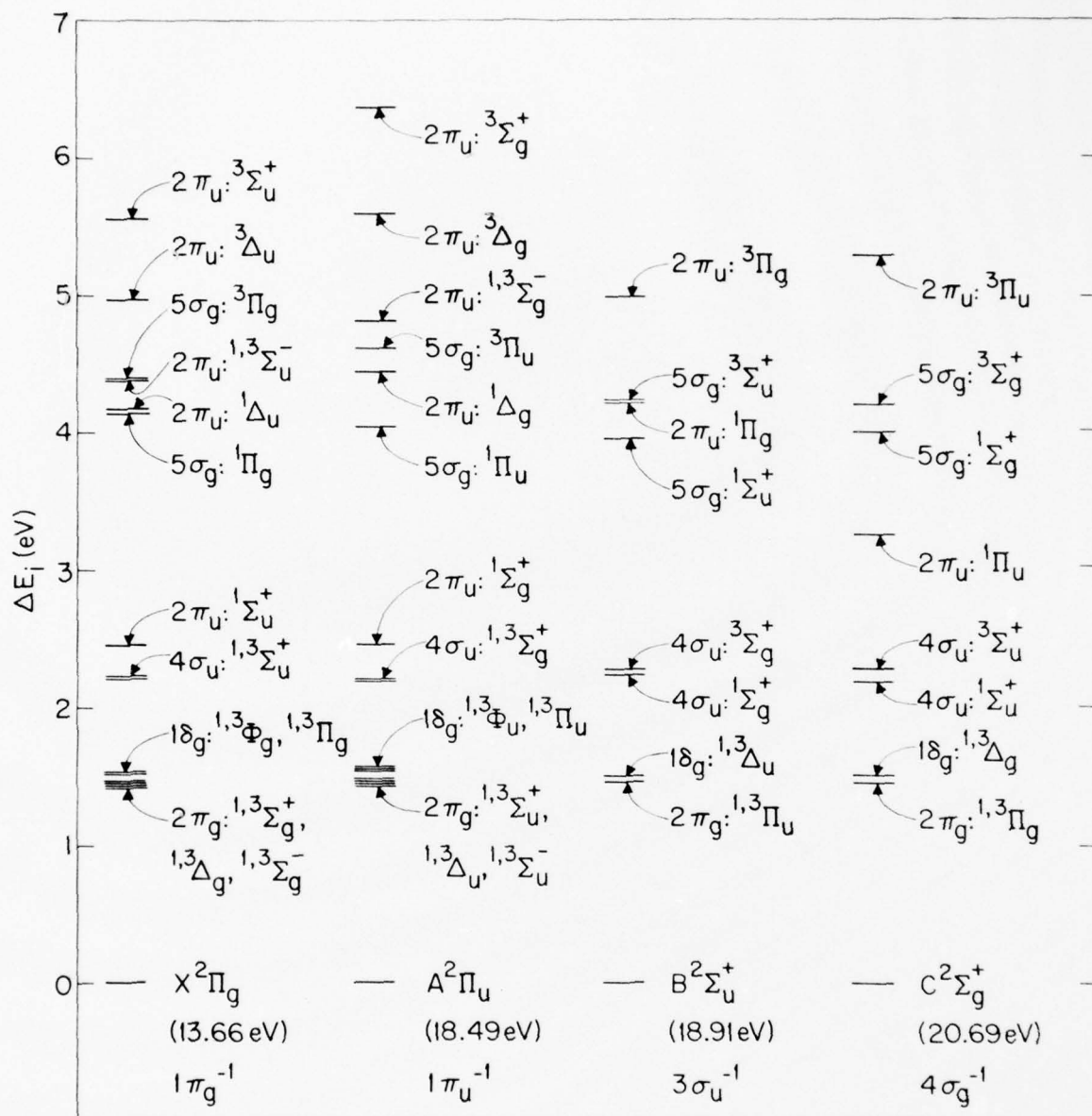


Fig. 4.

Vertical SCF Spectrum of Neutral CO_2 Relative to the Four Lowest States of CO_2^+ .

OZONE AND ITS IONS

A. Introduction

Experimentally, there are two states connected by dipole-allowed transitions to the ground 1A_1 state of ozone.^{1,2} The Chappuis band is assigned to the 1B_1 state, and the Hartley band is assigned to the 1B_2 state. In addition, the Huggins band has been attributed to the non-vertical part of the $^1B_2 \leftarrow ^1A_1$ transition, while the Wulf band has been assigned to the dipole-forbidden $^1A_2 \leftarrow ^1A_1$ transition. Recent electron energy loss spectroscopy has been used to detect the existence of at least one bound low-lying triplet state.³ The electronic spectra beyond the Hartley band has been reported,¹ including the electron energy loss spectra for an energy loss range of 1-30 eV.⁴ A variety of *ab initio* methods (self-consistent field, generalized valence-bond, and configuration interaction) have been used to compute the electronic spectra of ozone.⁵⁻⁸ Three states were found to be bound and a total of eight states had excitation energies lower than 6 eV.⁸

The spectra of O_3^+ has been studied by the high resolution photoelectron spectroscopy of ozone.⁹⁻¹¹ Three bands, between 12 and 14 eV, with accompanying vibrational structure were identified and attributed to ionization from the $6a_1$, $1a_2$ and $4b_2$ orbitals. Two studies¹⁰⁻¹¹ assigned the order of the ion states as X^2A_1 , A^2A_2 , B^2B_2 , whereas the third study⁹ assigned the ordering X^2A_1 , A^2B_2 , B^2A_2 . Koopmans' Theorem incorrectly predicts the ground state of O_3^+ to be 2A_2 , with the discrepancy arising not from differential orbital relaxation effects but from differences in the correlation energies of the ionic states.¹² Multi-configuration self-consistent field/configuration interaction

calculations¹³ support the assignment of the first two excited states as A^2A_2 , B^2B_2 , whereas the more extensive generalized valence-bond/configuration interaction calculations⁸ yields an ordering of A^2B_2 , B^2A_2 . The photoelectron spectra all show additional broad bands at higher energies corresponding to ionization from inner orbitals followed by shake-up processes, with all three studies differing on the number and orbital-state assignments of such bands. The *ab initio* calculations also disagree with each other (as well as with experiment) on the assignment of the higher states of O_3^+ .

Matrix isolation spectroscopy has been used to study the vibrational and electronic spectroscopy of the O_3^- ozonide ion.^{14,15} In addition, the electronic absorption and resonance Raman spectra of O_3^- have been studied by means of γ -irradiated spectra of alkali-metal halates.^{16,17} Only one electronic transition is observed for O_3^- and is assigned as $^2A_2 \leftarrow X^2B_1$.¹⁴ A variety of experimental techniques (charge transfer reactions,^{18,19} lattice energy calculations,²⁰ collisional ionization,²¹ drift-tube photodetachment^{22,23}) as well as an *ab initio* configuration interaction calculation²⁴ have been used to determine the electron affinity of ozone, and the consensus of results indicates a value of ~ 2.0 - 2.1 eV.

B. OZONE

Ab initio self-consistent field (SCF) and multi-configuration self-consistent field/configuration interaction (MCSCF/CI) calculations were performed on the lowest singlet and triplet states of O_3 at a single geometry corresponding to the experimental equilibrium geometry of the ground 1^1A_1 state ($R_{0-0} = 1.2717 \text{ \AA} = 2.403 a_0$, $\theta =$

116.78°)²⁵. Based on earlier SCF calculations,²⁶ the manifold of states of a given symmetry which result from various occupancies of the $6a_1$, $4b_2$, $2b_1$ and $1a_2$ valence orbitals are all quite close in energy. Thus a priori selection of the dominant Hartree-Fock configuration for a given state is not possible, and it is necessary to compute energies for several configurations of the same symmetry in order to determine the lowest one.

The computed SCF and MCSCF/CI vertical excitation energies for the valence states of O_3 are given in Table I. An examination of the SCF results reveals that the 3B_2 state is incorrectly predicted to be the ground state at this level of computation; this incorrect state ordering was also found in other theoretical calculations.⁸ Moreover, there is a reordering of some of the other excited states. The including of correlation energy results in a correct ordering of the 1A_1 and 3B_2 states. The present MCSCF/CI excitation energies are within the reported experimental range of energies for the observed transitions. It should be noted that the order and position of the electronic states of O_3 can be expected to vary significantly with geometry, even to the extent of inverting the ground and excited states.⁸

C. POSITIVE ION O_3^+

SCF and MCSCF/CI calculations were performed on the lowest doublet and quartet states of O_3^+ at the experimental equilibrium geometry of the X^1A_1 state of O_3 . The results of the vertical excitation energies are given in Table II. On theoretical grounds we expect O_3^+ to have an energy surface behavior comparable to NO_2 . Although Koopmans' Theorem predicts the ground state of O_3^+ to be 2A_2 , the

experimental ground state of the isoelectronic NO_2 molecule is $^2\text{A}_1$.¹ Once again the SCF calculations do not yield the correct ground, as also found in other theoretical works.^{12,13} Including correlation energy results in the correct ground state and shows the first excited state to be $^2\text{B}_2$.

The computed three lowest ionization potentials of O_3 are given in Table III, and are compared with experimental results. The MCSCF/CI values are all in error by 1.5-1.8 eV. We presently attribute the large errors in our calculated ionization potentials to restrictions in the present level of our computational method.

D. NEGATIVE ION O_3^-

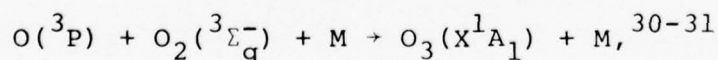
SCF and MCSCF/CI calculations were performed on the lowest doublet and quartet states of O_3^- at the experimental equilibrium geometry of the X^1A_1 state of O_3 . Previous experimental¹⁴ and theoretical²⁴ studies estimate the equilibrium geometry of the X^2B_1 state of O_3^- to be near that of the ground state of the neutral molecule. The computed vertical excitation energies are given in Table IV. In contrast to what was found for the O_3 and O_3^+ systems, SCF calculations are sufficient for a correct prediction of the ground state of O_3^- . The results for the quartet vertical excitation energies must be viewed with caution since these states are unstable in the SCF approximation. The MCSCF/CI calculation is in error by ~ 1 eV with the one experimentally observed transition, $^2\text{A}_2 \leftarrow \text{X}^2\text{B}_1$. The present results would seem to better support an assignment of $^2\text{A}_1 \leftarrow \text{X}^2\text{B}_1$, but deficiencies in the computations preclude any reassignments at the present time. It should also be noted that the

electronic spectra of O_3^- were studied in an argon matrix, not in the gas phase; thus the value of the measured transition energy may be significantly affected by environmental interactions. The computed SCF electron affinity exceeds the experimental values by ~ 0.3 eV, while the use of correlated wavefunctions, in their present level, fails to bind the electron to ozone.

E. FUTURE GOALS

Future work will deal with the extension of present levels and types of computational procedures in order to more accurately calculate energy quantities, especially energy differences between systems having different numbers of electrons (e.g., ionization potentials, electron affinity). A primary objective of this work will be the assignment of the high energy bands in the photoelectron spectra of O_3 , as well as the prediction of some yet unobserved transitions in the O_3^- ozonide ion.

We also propose to compute portions of the potential energy surface of the X^1A_1 state of ozone, with the principal emphasis in the well region to compute bound vibrational levels and spectroscopic constants. The vibrational deactivation of $O_2(^3\Sigma_g^-)$ by $O(^3P)$,²⁷⁻²⁹ and the three body recombination process,



are additional topics of interest involving the ground state potential surface.

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Table I. Vertical excitation energies for O_3 , $R_{0-0} = 2.403 \text{ a}_0$, $\theta = 116.8^\circ$.^a

State	SCF	MCSCF/CI	Expt. b,c
X^1A_1	1.7	0.0	0.0
1^1A_2	3.2	2.1	1.2-2.0
1^1B_1	3.5	2.3	2.0-2.3
1^1B_2	5.9	5.4	4.1-5.7
1^3A_1	7.5	8.0	
1^3A_2	2.8	2.0	
1^3B_1	2.7	1.9	
1^3B_2	0.0	1.6	

^aAll energies in electron volts.

^bG. Herzberg, *Molecular Spectra and Molecular Structure*, (Van Nostrand, 1967), Vol. 3.

^cM. Griggs, J. Chem. Phys. 49, 857 (1968).

Table II. Vertical excitation energies for O_3^+ , $R_{0-0} = 2.403 \text{ a}_O$,
 $\theta = 116.8^\circ$.^a

State	SCF	MCSCF/CI
X^2A_1	3.8	0.0
1^2A_2	0.7	0.5
1^2B_1	5.6	3.2
1^2B_2	3.8	0.1
1^4A_1	1.7	1.9
1^4A_2	0.0	2.7
1^4B_1	4.9	4.9
1^4B_2	1.0	1.4

^aAll energies in electron volts.

Table III. Vertical ionization potentials of O_3 , $R_{0-0} = 2.403 \text{ a}_O$, $\theta = 116.8^\circ$.^a

Orbital	State	SCF	MCSCF/CI	Expt. b,c,d
6a ₁	x ² A ₁	13.8	11.3	12.75
4b ₂	1 ² B ₂	13.8	11.4	13.03
1a ₂ ^e	1 ² A ₂	10.8	11.8	13.57

-46-

^aAll energies in electron volts.

^bJ. M. Dyke, L. Golob, N. Jonathan, A. Morris, and M. Okuda, J. Chem. Soc. Faraday Trans. II, 70, 1828 (1974).

^cD. C. Frost, S. T. Lee, and C. A. McDowell, Chem. Phys. Lett. 24, 149 (1974).

^dC. R. Brundle, Chem. Phys. Lett. 26, 25 (1974).

^eThe dominant HF configuration, as used in the SCF calculation, for the ²A₂ state does not correspond to simple ionization from the 1a₂ orbital, but rather to an ionization plus shake-up process.

Table IV. Vertical excitation energies for O_3^- , $R_{0-0} = 2.403 a_0$,
 $\theta = 116.8^\circ$.^a

State	SCF	MCSCF/CI	Expt. ^b
X^2B_1 ^c	0.0(2.4)	0.0(-0.5)	0.0(1.47-2.1) ^{d-j}
1^2A_1	2.6	2.7	
1^2A_2	4.2	3.7	2.8
1^2B_2	2.9	2.9	
1^4A_1	10.1	10.8	
1^4A_2	9.0	8.3	
1^4B_1	9.3	8.3	
1^4B_2	7.3	8.3	

^aAll energies in electron volts.

^bM. E. Jacox and D. E. Milligan, J. Mol. Spectry. 43, 148 (1972).

^cNumber in parentheses is the electron affinity.

^dJ. Berkowitz, W. A. Chupka, and D. Gutman, J. Chem. Phys. 55, 2733 (1971).

^eE. E. Ferguson, Can. J. Chem. 47, 1815 (1969).

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^hR. Byerly, Jr., and E. C. Beaty, J. Geophys. Res. 76, 4596 (1971).

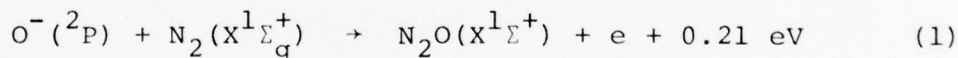
ⁱS. F. Wong, T. V. Vorburger, and S. B. Woo, Phys. Rev. A5, 2598 (1972).

^jM.M. Heaton, A. Pipano, and J.J. Kaufman, Int. J. Quantum Chem. S6, 181 (1972).

NITROUS OXIDE AND ITS NEGATIVE ION

A. Introduction

The N_2O , N_2O^- molecules are isoelectronic with the systems CO_2 , CO_2^- , respectively, and the Walsh-Mulliken rules^{1,2} predict that linear and bent geometries play important roles in N_2O , N_2O^- chemistry. The ground state $\text{N}_2\text{O}/\text{N}_2\text{O}^-$ prediction is that the minimum geometry of N_2O is linear, and the minimum geometry of ground state N_2O^- is bent. As was the case in the CO_2 , CO_2^- molecules, the potential energy surfaces intersect, with the ground state potential energy surface of N_2O lying lowest for geometries near the linear equilibrium geometry of N_2O , and with the ground state potential energy surface of N_2O^- lying lowest near the bent equilibrium geometry of N_2O^- . The details of these surfaces and their intersection bear directly on the possible ionospheric associative detachment reaction



which has not been observed in laboratory experiments conducted at 300K. A low thermal rate constant has been assigned to Reaction (1) by several experimenters,³⁻⁶ and conflicting reports exist^{6,7} concerning reactivity above 0.3 eV relative collision energy (ground vibrational state N_2).

The low thermal rate constant for the exothermic Reaction (1) suggests that substantial barriers are involved in the intersection of the N_2O and N_2O^- potential energy surfaces, and that vibrationally excited reagent N_2 may appreciably enhance the reaction. Since vibrationally excited N_2 is common in the ionosphere, the characterization of the N_2O and N_2O^- potential surfaces, needed to predict the

effects of vibrationally hot reagent N_2 on the rate of Reaction (1), warrants detailed investigation.

B. The Ground State N_2O and N_2O^- Potential Energy Surfaces

Thermodynamic cycles can be constructed which express the adiabatic electron affinity of N_2O , $EA(N_2O)$, and the dissociation energy of the $N-NO^-$ bond in N_2O^- , $D(N-NO^-)$, in terms of known thermodynamic quantities:

$$EA(N_2O) = EA(O) + D(N_2-O^-) - D(N_2-O) \quad (2a)$$

$$D(N-NO^-) = EA(N_2O) + D(N-NO) - EA(NO) \quad (2b)$$

The values used are shown in Table 1, together with the resulting $EA(N_2O)$ and $D(N-NO^-)$ values.

Ab initio self-consistent-field (SCF) and multiconfiguration self-consistent-field, followed by configuration interaction (MCSCF/CI), wavefunction calculations were performed to determine the potential energy surfaces for N_2O and N_2O^- . Equilibrium geometries and harmonic force constants and vibrational frequencies are shown in Table 2. It follows from these results that the shapes of the N_2O and N_2O^- potential energy surfaces should be reliably determined near their respective minima.

Ab initio bending and stretching potentials can be used to estimate the energy required to change the geometry of N_2O^- from its equilibrium value to that of equilibrium N_2O . The computed values are listed in Table 3. The predicted barrier, 2.5 eV, is significantly higher than the exothermicity of Reaction (1), in support of a low thermal rate constant.

The intersection locus of the ground state N_2O^- and N_2O potential energy surfaces can be determined by fitting the *ab initio* N_2O and N_2O^- potential energy points with a functional form. It was found that a two-dimensional anharmonic Morse potential form was sufficient, in which one bondlength is treated parametrically. The anharmonicity is essential for close reproduction of the *ab initio* N_2O vertical electron affinity. The minimum energy of intersection between the N_2O and N_2O^- potential surfaces is found to be ~ 0.66 eV above the potential energy of equilibrium geometry N_2O . The geometry at the minimum energy of intersection is

$$R_{NO} = 1.28 \overset{\circ}{\text{\AA}} \quad (3a)$$

$$R_{NN} = 1.18 \overset{\circ}{\text{\AA}} \quad (3b)$$

$$\angle(NNO) = 155^\circ \quad (3c)$$

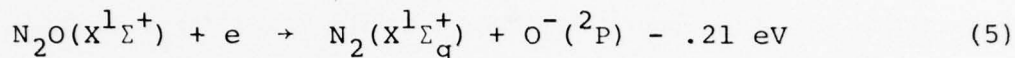
The associative detachment threshold for Reaction (1) is obtained from the minimum energy intersection by adding the zero point energy of the minimum intersection energy complex and subtracting 1) the asymptotic $N_2 + O^-$ energy obtained from the anharmonic Morse form, and 2) the zero point energy of N_2 . The predicted threshold for Reaction (1) is

$$E_a(\text{Rxn 1}) = 0.21 \text{ eV} \quad (4)$$

This activation energy is less than the energy necessary to excite reagent N_2 to the first excited vibrational state (0.29 eV). Furthermore, the R_{NN} of Equation (3b) is greater by $0.04 \overset{\circ}{\text{\AA}}$ than the classical anharmonic turning point for vibrationally cold N_2 ($1.146 \overset{\circ}{\text{\AA}}$), and almost equal to the outer turning point for N_2 in its first excited vibrational state ($1.185 \overset{\circ}{\text{\AA}}$). Thus, the rate of Reaction (1)

will probably not be enhanced by translational excitation of vibrationally cold N_2 , but may be strongly enhanced by vibrational excitation of reagent N_2 , with or without translational excitation.

The N_2O and N_2O^- potential energy surface intersection also provides information for the dissociative attachment threshold



The electron detachment threshold for Reaction (5) is obtained from the minimum energy intersection by adding the zero point energy of the minimum intersection energy complex, and subtracting 1) the N_2O equilibrium potential energy, and 2) the zero point energy of N_2O . The result is

$$E_a(\text{Rxn}(5)) = 0.40 \text{ eV} \quad (6)$$

which is in good agreement with the experimental estimate of 0.45 eV.⁸ Since the minimum intersection occurs with extended bondlengths relative to equilibrium N_2O , and at an angle about 25° away from linearity, it is very likely that the electron detachment described by Reaction (4) will be facilitated by excitation of the N_2O bending and symmetric stretch modes.

The vertical electron affinity, or resonance energy, for $N_2O(^1\Sigma^+)$ can be reliably obtained from the previously computed adiabatic electron affinity by adding the zero point energy of N_2O^- , and subtracting 1) the zero point energy of $N_2O^-(^2\Pi)$, which is estimated to be the same as the N_2 zero point energy, 2) the barrier to bending, and 3) the barrier to contraction of the bondlengths. A vertical electron affinity of -2.23 eV results, which is in good agreement with broad experimental electron scattering peaks.⁹

C. Conclusions

The ground state potential energy surface of N_2O^- is stable in its equilibrium region to both associative detachment (Reaction (1)) and dissociation. The features of the ground state $\text{N}_2\text{O}/\text{N}_2\text{O}^-$ potential surfaces described in this report show why this is so. Associative detachment is immeasurably slow for reagent thermal N_2 because there is a barrier of ~ 0.2 eV which the reagents must overcome to reach the minimum intersection energy of the $\text{N}_2\text{O}/\text{N}_2\text{O}^-$ surfaces. Moreover, the minimum intersection occurs at R_{NN} bond-lengths greater than the equilibrium N_2 bondlength, which suggests that vibrationally hot N_2 will be needed to effectively enhance reaction.

The dissociative attachment process (Reaction (5)) is likewise described by the $\text{N}_2\text{O}/\text{N}_2\text{O}^-$ potential surfaces. The N_2O molecule must be vibrationally excited in order to reach the minimum energy of intersection of the $\text{N}_2\text{O}/\text{N}_2\text{O}^-$ surfaces. This requires at least the absorption of several bending vibrational quanta. Here, however, the threshold energy (0.4 eV) is sufficient to populate these levels. Since the minimum intersection energy involves slightly longer R_{NN} and R_{NO} than occur in N_2O , it is likely that the excitation of stretching vibrational quanta will further enhance reaction.

Our results also provide a vertical electron affinity of -2.23 eV for $\text{N}_2\text{O}(^1\Sigma^+)$. This value is thought to be reliable, since it was obtained with a method which does not involve a nonvariational determination directly.

D. Future Goals

There is evidence from experimental^{10,11} and theoretical^{12,13} studies that a major source of N_2 vibrational temperature in the upper atmosphere is its $E \rightarrow V, R, T$ energy transfer reaction with $O(^1D)$. The vibrational temperature of N_2 is important because it strongly influences important atmospheric characteristics such as electron density and temperature, and the quantity of infrared radiation from CO_2 , H_2O , etc. The intersection of excited N_2O triplet surfaces with the ground state singlet N_2O surface will be determined, since these are central to understanding the vibrational deactivation of N_2 by $O(^1D)$. Preliminary SCF computations in our laboratory indicate that correlated MCSCF/CI wavefunctions are needed for these surfaces.

The reaction to form $NO^+(X^1\Sigma^+) + N(^4S)$ from $O^+(^4S) + N_2(X^1\Sigma^+)$ determines the free electron depletion rate in the ionosphere.¹⁴ The understanding of this reaction involves the intersection of excited N_2O^+ quartet surfaces with the ground state N_2O^+ doublet surface. We shall investigate these in detail, since there may be reaction barriers which affect the accessible paths.

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Table 1. Bond dissociation energies and electron affinities for the N_2O/N_2O^- systems.
Units are eV.

$D(N_2-O)^a$	$D(N-NO)^a$	$EA(O)^b$	$EA(NO)^c$	$D(N_2-O^-)^d$	$EA(N_2O)^e$	$D(N-NO^-)^f$
1.68	4.93	1.47	0.02	0.43	0.22	5.13

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^eEquation (2a) of text

^fEquation (2b) of text

Table 2. *Ab initio* potential energy surface characteristics for N_2O^- and N_2O .

Parameter	N_2O^-		N_2O	
	SCF	MCSCF/CI	MCSCF/CI	Expt.
$R_{NN}^e (\text{\AA})$	1.204	1.222	1.147	1.128 ^a
$R_{NO}^e (\text{\AA})$	1.376	1.375	1.240	1.184 ^a
$\angle NNO (\text{deg})$	123.6	132.68	180	180 ^a
$k_{NN} (\text{md/\AA})$	11.54	11.49	17.21	17.88 ^b
$k_{NO} (\text{md/\AA})$	3.93	3.83	9.99	11.39 ^b
$k_{NNO} (\text{md/\AA})$	0.645	0.643	0.41	0.49 ^b
$\nu_{NO} (\text{cm}^{-1})^c$	945	912	1223	1285 ^a
$\nu_{NNO} (\text{cm}^{-1})^c$	535	555	524	589 ^a
$\nu_{NN} (\text{cm}^{-1})^c$	1660	1666	2183	2224 ^a
$\epsilon_O (\text{eV})^d$	0.196	0.195	0.245	0.254 ^a

^aG. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules" (Van Nostrand Reinhold, New York, 1966).

^bE. B. Wilson, J. C. Decius, and P. C. Goss, "Molecular Vibrations" (McGraw-Hill, New York, 1955).

^cAtomic masses are $m_N = 14.00751$, $m_O = 16.0000$

^dZero point energy.

Table 3. Bending and stretching barriers for N_2O^-

	SCF	MCSCF/CI
$\Delta E_b(\text{eV})^a$	1.41	1.10
$\Delta E_s(\text{eV})^b$	-1.00	-1.40
$\Delta E(\text{eV})^c$	2.41	2.50

^aEnergy rise upon bending \angle (NNO) from the bent equilibrium value to 180° . Bondlengths are equal to their equilibrium values.

^bEnergy change upon stretching the NN and NO bondlengths from their equilibrium N_2O values to their equilibrium N_2O^- values.

^c $\Delta E = \Delta E_b - \Delta E_s$

IONS OF NITROGEN DIOXIDE

A. Introduction

High resolution photoelectron spectra for NO_2 are known for energies up to 27.5 eV.^{1,2} The NO_2^+ ion peaks have been assigned on the basis of ground state NO_2^+ calculations and by analogy with the isoelectronic CO_2 molecule.²⁻⁴ No definitive experimental assignment of the first ionization potential has been made, owing to the great difference between the neutral (bent) and ion (linear) equilibrium geometries.

Semiempirical calculations on NO_2^- ^{5,6} are in essential agreement with a number of experiments dealing with absorption spectra in NaNO_2 or phosphorescence in aqueous solutions. Polarization studies have assigned the electric dipole allowed $^1\text{B}_1$ state in the region just under 3 eV.^{7,8} The $^3\text{B}_1$ state has been assigned to ~2.4 eV.⁹⁻¹¹ The $^1\text{A}_2$ state was calculated to be ~4.5 eV semiempirically,⁵ and on this basis spectral assignments made.^{10,12,13} The $^1\text{B}_2$ state is dipole allowed, and lies about 6 eV above X^1A_1 .^{5,12}

B. Neutral NO_2

The most accurate theoretical results available for NO_2 were previously calculated in this laboratory.¹⁴ We use these to evaluate our present efforts for the singly charged ions. The vertical NO_2 spectrum we compute agrees with the accurate results to within ~0.6 eV. To the extent that NO_2 is representative of NO_2^+ and NO_2^- , a comparable accuracy of the ionic spectra is expected.

C. Positive Ion NO₂⁺

Vertical excitation energies for NO₂ ($R_{\text{NO}} = 2.25$ bohrs, $\angle \text{ONO} = 134^\circ$) were computed with single- and multiconfiguration self-consistent-field methods (SCF and MCSCF methods). Configuration interaction was then carried out using the MCSCF results (MCSCF/CI). The computed and experimental spectra are compared in Table 1. The SCF results predict the wrong first ionization potential (³B₂ instead of ¹A₁), but otherwise are in reasonable agreement with the MCSCF/CI spectrum. The MCSCF/CI spectrum is somewhat different from the experimental spectrum, and this may in part be due to the difference between theoretically computed vertical ionizations and those obtained by subtracting experimental photoelectron spectral peaks. This is probable for molecules like NO₂/NO₂⁺, where ground state neutral and ion equilibrium geometries are very different. Because of these geometry differences, vibrationally excited levels can be expected to be observed in the experiments, and these are not included in theoretical calculations such as ours.

A linear to bent geometry NO₂⁺ correlation diagram is drawn on Figure 1. The energies represented by solid lines are SCF energies. The dashed lines represent MCSCF variational estimates of states which collapse variationally in the SCF model. The dotted line shown for (¹B₂) should not be taken too seriously, since it is a guess made on the basis of the Walsh-Mulliken rules,¹⁵⁻¹⁶ and was not observed in our computed results. The linear NO₂⁺ SCF spectrum appears to be correctly ordered, and clearly shows the greater stability of the linear ground state. However, the beha-

behavior of the states introduced by bending is not like that observed in CO_2 , and this is possibly significant because in the past orderings, etc., have been rationalized by assuming CO_2 is a reasonable model for NO_2^+ .

D. Negative Ion NO_2^-

Computed SCF vertical excitation energies ($R_{\text{NO}} = 2.25$ bohrs, $\angle \text{ONO} = 134^\circ$) and experimental excitation energies for NO_2^- are shown in Table 2. Qualitative agreement is observed between the SCF and experimental spectra, but quantitative differences are obvious. Reasons for the quantitative differences may in part be due to differences between the vertical geometry and the experimental geometry. For example, the $\angle \text{ONO}$ for the minimum X^1A_1 geometry may be $\sim 116^\circ$ ^{17,18} as opposed to the vertical value $\angle \text{ONO} = 134^\circ$. Another possible reason is that the SCF method is not totally appropriate for the kinds of vertical electron attachments that occur in forming NO_2^- from NO_2 .

An adiabatic correlation diagram for NO_2^- is drawn on Figure 2. The C_{2v} energy levels are those reported in Table 2. The diagram on Figure 2 is the first for NO_2^- that is based on *ab initio* energy levels.

According to the correlation diagram, electron attachment in the range $\sim 0-1$ eV is associated with only two states, 3B_1 and X^1A_1 . Structure which is observed below 1 eV should be associated with the ground state, in agreement with experimental conclusions.¹⁹⁻²¹ Dissociative attachment of electrons has produced each of the species O^- , O_2^- and NO^- .²²⁻²⁴ The appearance potentials for each are

about the same as their thermodynamic thresholds. The adiabatic paths on Figure 2 likewise suggest no apparent barriers. The production of O^- is observed to be largest,²² and this agrees with the fact that several adiabatic paths on Figure 2 provide routes to the lowest energy asymptote, which produces O^- . However, non-adiabatic interactions must occur for the case of NO^- production.

E. Future Goals

The SCF linear to bent geometry correlation diagrams for NO_2^+ and CO_2 which we have computed in the present work suggest that the isoelectronic CO_2 and NO_2^+ molecules behave differently in a qualitative sense. We shall determine whether this difference prevails in more accurate descriptions. Several of the states which enter in NO_2^+ Walsh rules will also be computed in order to furnish a completely *ab initio* correlation diagram. The extended and more accurate descriptions of NO_2^+ will also be needed to further understand the difference between theory and experiment, if indeed this difference persists.

Negative ion NO_2^- energy levels which include electron correlation, as well as different bending angles, are likewise needed to clarify the differences between theory and experiment. In this respect NO_2^- is a good candidate system, since it is variationally stable relative to NO_2 in many states, and since, experimentally, optically allowed transitions are low-lying in the NO_2^- spectrum.

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Table 1. Vertical excitation energies for NO_2^+ , $R_{\text{NO}} = 2.24$ bohrs,
 $\angle \text{ONO} = 134^\circ$. Units are eV.

Ion State	SCF	MCSCF/CI	Expt. ^a
1A_1	0.90	0.00	0.00
3B_2	0.00	2.56	1.78
3A_2	1.34	2.65	2.37
1A_2	1.78	3.55	2.83
1B_2	4.13	3.84	3.28
3A_1	7.28	6.83	6.22
3B_1	8.27	7.70	6.41
1B_1	9.28	8.78	-

^aC. R. Brundle, D. Neumann, W. C. Price, D. Evans, A. W. Potts,
and D. G. Streets, J. Chem. Phys. 53, 705 (1970).

Table 2. Excitation energies for NO_2^- , $R_{\text{NO}} = 2.25$ bohrs, $\angle \text{ONO} = 134^\circ$. Units are eV.

Ion State	SCF ^a	Expt. ^b
$^1\text{A}_1$	0.00	
$^3\text{B}_1$	0.98	$\sim 2.4^{\text{c-e}}$
$^1\text{B}_1$	2.47	$\sim 3^{\text{f,g}}$
$^3\text{B}_2$	4.12	
$^3\text{A}_2$	5.60	
$^1\text{A}_2$	5.92	$\sim 4.5^{\text{h}}$
$^1\text{B}_2$	8.26	$\sim 6^{\text{d,i,j}}$
$^3\text{A}_1$	9.62	

^aVertical

^bAdiabatic

^cH. J. Maria, A. Wahlborg, and S. P. McGlynn, J. Chem. Phys. 49, 4925 (1968).

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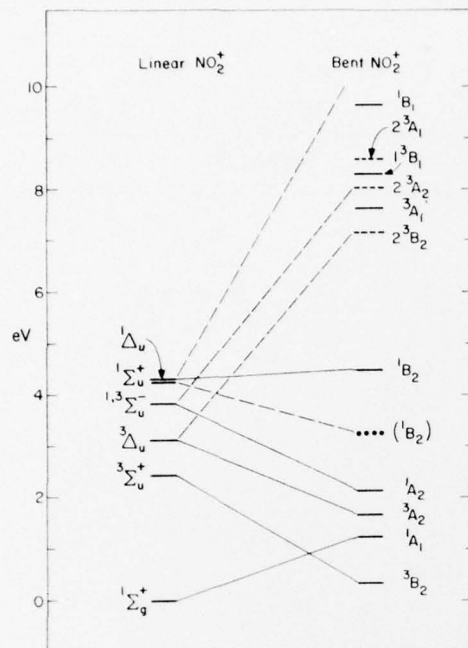
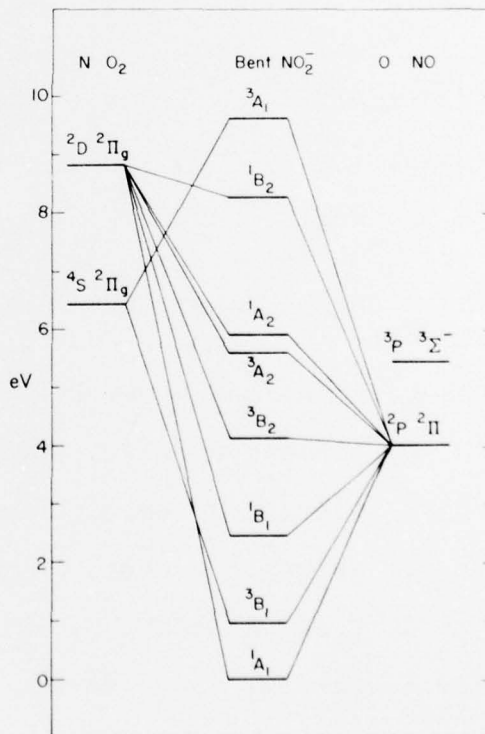


Fig. 1.

State Correlation Diagram for Linear and Bent NO^+ . The Solid Lines are SCF Energy Levels. The Dashed Lines are Variational MCSCF Values for Higher Roots of a Given Symmetry. The Dotted Value is an Estimate Based on the Walsh-Mulliken Rules, and was not Computed *ab initio*. The Energy Zero is $\text{NO}_2^+(1\Sigma_g^+)$ as Given by the SCF Model.

Fig. 2.

State Correlation Diagram for NO_2^- . The Molecular Ion Energies are SCF Values. The Asymptote Energies were taken from "Potential Energy Surfaces for Air Triatomics," M. Krauss, D. G. Hopper, P. J. Fortune, A. C. Wahl, and T. O. Tiernan, ARL TR 75-0202, Vol. 1. The Energy Zero is $\text{NO}_2^-(1A_1)$ as Given by the SCF Model.



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